Physical Chemistry

Academician A. N. FRUMKIN, R. I. KAGANOVICH, E. V. YAKOVLEVA

1961

SovietRxiv

Abstract

Full Text

Physical Chemistry

Academician A. N. FRUMKIN, R. I. KAGANOVICH, E. V. YAKOVLEVA
and V. V. SOBOL

THE INFLUENCE OF CATIONS ON OXYGEN OVERVOLTAGE

The influence of the nature of cations on anodic reactions has been observed in the case of a number of electrochemical processes occurring at high anodic potentials.

N. A. Izgaryshev and co-workers (1) studied the dependence of the yield of persulfates and perchlorates on the nature of the cations. In these works the influence of cations was explained by their dehydrating action on anions, which depended on the radius and hydration energy of the cations. K. L. Il’ in (2) explained the influence of cations on the results of electrolysis of chlorides in neutral media (without a diaphragm) by the different solubility of the electrolysis products. T. Erdey-Gruz and I. Shafarik (3) were the first to indicate the adsorption nature of the influence of cations on oxygen overvoltage. They assumed that cations, being attracted to adsorbed SO_4^{2-} anions, affect the discharge process of water molecules by deforming them on the electrode surface. Chu Yu-tsao and Mi Tien-yin (4) drew attention to the connection between the kinetics of the persulfate-formation process and the rate of oxygen evolution, and indicated the range of potentials in which the strongest influence of cations on oxygen overvoltage is observed.

An action of cations similar to that observed during oxygen evolution on platinum was found by M. Ya. Fioshin, Yu. B. Vasil’ ev, and E. G. Gaginkina (5) in the electrolysis of acetate solutions.

In the present work, results are presented from a study of the influence of certain cations on oxygen overvoltage in solutions of sulfuric and perchloric acids. Of special interest is the investigation of the reaction of oxygen evolution from perchloric acid solutions, which over a fairly wide interval of potentials is not complicated by side processes.

Polarization curves were recorded in a cell with anodic and cathodic compartments separated by a glass filter. The anode was a platinum wire of diameter $95\,\mu$ and area 10^{-2} cm^2. A platinum wire in the form of a spiral was also used as the cathode. Potentials were measured with respect to a hydrogen electrode in the same solution. The hydrogen electrode was connected to the anode by an electrolytic bridge terminating in a capillary sealed into the anodic compartment. In addition to the usual polarization curves, i–φ curves were recorded by the method described in (^{6}), as well as curves of the potential decay after interruption of the current.

Before the curves were recorded, the anode was treated with dilute nitric acid and concentrated sulfuric acid, washed with water, and then anodically polarized for 30 min with a current of $6 \cdot 10^{-6}$ A in $1\,N$ H_2SO_4. When the polarization curves were recorded, each point was held for 2 min to attain a constant potential. The acids and water used had been purified beforehand by double distillation, and the salts by recrystallization.

In perchloric acid solutions, the influence of additions of the perchlorates of Cs^+, K^+, and Ba^{2+} was investigated. In Fig. 1 the polarization curves are presented,

recorded in $1.34\,N$ $HClO_4$ with additions of Cs^+ and K^+ at various concentrations. From the curves in Fig. 1 it follows that the effect of these ions is manifested predominantly in the region of the abrupt increase in potential; only a very weak effect is also observed at higher polarizations. In the presence of cations the potential jump shifts toward lower current densities, and the activity of cesium exceeds the activity of potassium by almost an order of magnitude. With increasing cation concentration the transition from the lower to the upper branch of the polarization curve occurs more gradually; thus, in a solution containing K^+ at a concentration of $10^{-2}\,N$, intermediate points in the rising section of the curve also become accessible to measurement.

Fig. 1. Anodic polarization curves of a platinum electrode in solutions:
1 –$1.34\,N$ $HClO_4$;
2 –$1.34\,N$ $HClO_4$ + $8 \cdot 10^{-3}\,N$ $KClO_4$, and $1.34\,N$ $HClO_4$ + $10^{-3}\,N$ $CsClO_4$;
3 –$1.34\,N$ $HClO_4$ + $2.5 \cdot 10^{-3}\,N$ $CsClO_4$;
4 –$1.34\,N$ $HClO_4$ + $10^{-2}\,N$ $KClO_4$.

In Fig. 2 are shown i–φ curves obtained by applying to the electrodes a voltage increasing linearly with time through a low-resistance potentiometer at a rate of 8 mV/sec in pure $1.34\,N$ $HClO_4$ solution (1) and with additions of Cs^+ and K^+ (2 and 3). From the curves in Fig. 2 it is seen that in the potential region 2.5–2.9 V, in the solutions studied, a current decrease is observed, indicating a slowing of the oxygen-evolution process. The effect of the cations is expressed in a decrease in the current at a given potential; it appears most strongly at the potential of the current maximum and practically completely disappears on considerable departure from the latter. When the curves are recorded from higher current densities toward lower ones (curves 1′, 2′, 3′), a hysteresis loop is observed; in the region of potentials of the current decrease the "reverse-run" curve has a plateau.

Fig. 2. Anodic polarization curves of a platinum electrode, recorded with continuous variation of the applied potential in solutions: 1–$1.34\,N$ $HClO_4$; 2 –$1.34\,N$ $HClO_4$ + $2.5 \cdot 10^{-3}\,N$ $CsClO_4$; 3–$1.34\,N$ $HClO_4$ + $10^{-2}\,N$ $KClO_4$. Curves 1′, 2′, and 3′ were obtained in the same solutions during the reverse course of polarization.

Fig. 3

Figure 1: Fig. 3

Polarization curves recorded in 1.34 N $HClO_4$ solutions with additions of various concentrations of barium perchlorate are analogous to the curves obtained in the presence of Cs^+ and K^+ ions. Like these cations, the Ba^{2+} ion exerts the greatest influence in the region of rapid change of potential. However, if one compares the cation concentrations that cause a shift of the onset ⋯

of the onset of the potential jump, for example, at $i = 10^{-1}$ A/cm^2, it turns out that Cs^+ produces this shift at a concentration of $2.5 \cdot 10^{-3}$ N, K^+ at 10^{-2} N, and Ba^{2+} at $4 \cdot 10^{-1}$ N, i.e., cesium is almost 200 times more active than barium.

With an increase in the concentration of perchloric acid, the effect of cations on the oxygen overvoltage decreases. Thus, in 3 N $HClO_4$ a shift of the anodic potential is observed upon addition of Cs^+ at a concentration of 10^{-2} N. The K^+ ion at this acid concentration has no effect. In 5.8 N $HClO_4$, no effect even of Cs^+ cations was detected.

Fig. 3. Anodic polarization curves of a platinum electrode in solutions: 1 –5 N H_2SO_4; 2 –5 N H_2SO_4 + 10^{-2} N Cs_2SO_4; 3 –5 N H_2SO_4 + 10^{-1} N Cs_2SO_4; 4 –5 N $H_2SO_4 + 1$ N Cs_2SO_4

In a sulfuric acid solution, polarization curves were recorded with additions of sulfates of Cs^+, K^+, Na^+, and Li^+ at concentrations from 1 to 10^{-2} N. Figure 3 shows polarization curves recorded in 5 N sulfuric acid in the presence of cesium sulfate. For comparison, the polarization curve for pure 5 N H_2SO_4 is also given.

From Fig. 3 it is evident that the overall pattern of the phenomenon in the case of sulfuric acid is the same as in the case of $HClO_4$. However, the dependence of the magnitude of the cation effect on current density is much less sharply expressed, since the changes in the slope of the polarization curve themselves are also less sharply expressed.

The curves obtained in the presence of sulfates of K^+, Na^+, and Li^+ are analogous to the curves shown in Fig. 3. In order of decreasing influence on the anode potential, the cations studied may be arranged in the series:

$$Cs^+ > K^+ > Na^+ > Li^+.$$

As an example, Table 1 gives the values of the change in anode potential at a current density of $2 \cdot 10^{-1}$ A/cm^2 upon introducing the cations studied into a 5 N H_2SO_4 solution at various concentrations.

Table 1

Cation conc. in N	$\Delta\varphi$, V Cs^+	$\Delta\varphi$, V K^+	$\Delta\varphi$, V Na^+	$\Delta\varphi$, V Li^+
1	0.53	0.39	0.18	0.06
0.1	0.37	0.22	0.09	0.04
0.01	0.13	0.11	0.05	–

By the method of measuring potential-decay curves after switching off the current (^{7}), it was found that the capacitance of a platinum electrode C in 1.34 N $HClO_4$, upon transition from potentials corresponding to the lower branch of the polarization curve to potentials lying at the upper boundary of the jump, changes from 80–100 to 20 μF. The experimental procedure and calculation are set forth in more detail in (^{7}). Measurements carried out by us in the presence of Cs^+ and K^+ cations in a 1.34 N $HClO_4$ solution showed that the changes in capacitance are parallel to the changes in the polarization curves: as is evident from Fig. 4, the more active the cation, i.e., the more strongly the cation affects the oxygen overvoltage, the lower the capacitance values at which the drop is observed on the curves C–$\lg i$.

On the basis of the totality of the data obtained, the following explanation of the action of cations may be proposed, proceeding from the concepts of the nature of the potential jump set forth in (^{7}). The appearance on the surface of adsorbed oxygen atoms and chemisorbed anions, forming dipoles whose negative ends are directed toward the solution, creates the possibility of local adsorption of cations, despite the high positive potential of the electrode. In acid solutions, those located on the surf-

negative groups on the platinum surface attract hydrogen ions; it may be said that they acquire an acidic character. When cesium, potassium, or barium cations are introduced into the solution, the latter partially or completely replace the hydrogen ions. The degree of replacement evidently increases with increasing adsorbability and concentration of the cations and decreases with increasing activity of the acid hydrogen ions. Judging from the fact that the action of cesium is manifested in the presence of so considerable an excess of hydrogen ions, the difference in their adsorbabilities in this case is apparently greater than in the case of adsorption on the negatively charged surface of mercury. Replacement of the hydrogen ion by specifically adsorbed cations should increase the adsorption energy of anionic groups, just as the presence of cesium enhances the adsorption of iodine on the surface of mercury. The increase in adsorption energy apparently leads to strengthening of the surface chemisorbed layer and to a decrease in the rate of its decomposition with evolution of oxygen. As a result, filling of the surface is completed at lower current densities; at the same time, repulsion between adsorbed cations leads to the filling occurring in the presence of alkali-metal cations somewhat more gradually than in pure acid solutions.

Fig. 4. Curves of capacitance variation with current density for solutions: 1 –1.34 N $HClO_4$; 2 –1.34 N $HClO_4$ + 10^{-2} N $KClO_4$; 3 –1.34 N $HClO_4$ +

Fig. 4. Curves of capacitance variation with current density for solutions: 1 — 1.34 N $HClO_4$; 2 —1.34 N $HClO_4$ + 10^{-2} N $KClO_4$; 3 —1.34 N $HClO_4$ + $2.5 \cdot 10^{-3}$ N $CsClO_4$

Figure 2: Fig. 4. Curves of capacitance variation with current density for solutions: 1 —1.34 N $HClO_4$; 2 —1.34 N $HClO_4$ + 10^{-2} N $KClO_4$; 3 —1.34 N $HClO_4$ + $2.5 \cdot 10^{-3}$ N $CsClO_4$

$2.5 \cdot 10^{-3}$ N $CsClO_4$

The effect of a change in bond energy should be manifested most strongly under conditions where the filling approaches completion. Therefore, the influence of the cation is reflected primarily in the current density at which the potential jump occurs; moreover, the maximum filling of the surface with anionic groups creates the most favorable conditions for adsorption of cations. Further growth of the potential on the upper branch of the polarization curve should decrease adsorption of cations. The latter should also be somewhat less pronounced on the lower branch of the curve before the onset of the potential jump, owing to the lower concentration of anionic groups on the electrode surface.

Moscow State University
named after M. V. Lomonosov

Received
23 IX 1961

REFERENCES CITED

1. N. Isgarischew, S. Berkman, *Zs. Elektrochem.*, **28**, 40 (1922); N. A. Izgaryshev, M. G. Khachaturyan, *DAN*, **59**, 1125 (1948); N. A. Izgaryshev, A. A. Petrova, *ZhFKh*, **5**, 881 (1950); N. A. Izgaryshev, *Izv. AN SSSR, OKhN*, 1950, 15.

2. K. L. Il' in, *Tr. Novocherkassk. Politekhn. Inst.*, **34**, 33 (1956).

3. T. Erdey-Gruz, I. Shafarik, *Tr. IV Soveshch. po elektrokhim.*, Moscow, 1959, p. 263.

4. Tsu Yu-yuan, Min Tien-yin, *DAN*, **125**, 1069 (1959).

5. M. Ya. Fioshin, Yu. B. Vasil' ev, E. G. Gankina, *DAN*, **135**, 909 (1960).

6. R. I. Kaganovich, M. A. Gerovich, *ZhFKh*, **32**, 956 (1958).

7. A. N. Frumkin, V. V. Sobol' , *DAN*, **141**, No. 4 (1961).

Note: Figure translations are in progress. See original paper for figures.